The Ultramicroscopic Structure of Soaps.

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[Plates 10 and 11.]

In 1912, Bachmann* published, with Zsigmondy, beautiful pioneer descriptions of the ultramicroscopic appearance and behaviour of soaps. In view of our present greatly extended knowledge of the constitution of soap solutions, sols, gels, and curds, it was highly desirable to extend these morphological observations, and to correlate the various phenomena observed by Zsigmondy and Bachmann with the known constituents of these systems. It was also of great importance to find out to which state, whether sol, gel, or curd, the various phenomena were to be attributed. A further interest lay in the development of the technique of such investigations as, for instance, in the application of the cinematograph to the study of the life-history of an ultramicroscopic particle or formation in its genesis and subsequent transformations.

The present paper contains some novel information with regard to Brownian movement and the distinction between sols, gels, and curds, the three different states which are possible for soaps. Although we have given a year to this work, in each experiment with the ultramicroscope we still find some new detail. We have endeavoured to record only those observations which appear reproducible and characteristic.

States in which Aqueous Soap Solutions exist.

A "soap sol" is to be defined as a clear transparent liquid, whose viscosity may range from that of water up to a value several thousand times as great. Almost invariably there is to be found, floating in these otherwise clear solutions, a sediment of solid soap, the result of the small but definite amount of hydrolysis that is universally exhibited by all aqueous soap systems. Often, again, at lower temperatures, the soap solution deposits the soap which is present in excess of the solubility corresponding to that temperature.

A "soap gel" is a clear transparent body which is identical with a soap sol in every respect, except that it retains a definite form and possesses elasticity. Often a gel is clouded by the formation of a few true curd fibres.

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* 'Kolloid-Zeitschr.,' vol. 11, p. 150.

A "soap curd" is a white, more or less opaque, mass. It consists of innumerable curd fibres, enmeshed in which is a soap gel or sol. The concentration of the gel or sol depends upon the temperature and upon the nature of the soap, varying from very high concentration to practically pure water, the latter being the case for the more insoluble sodium soaps of the highest saturated fatty acids.

Finally, in the case of the potassium soaps, there may co-exist with one or more of the above systems transparent tabular crystals of hydrated potassium soap.

The above relationships and types have not hitherto been recognised or described. Their elucidation is primarily the work of Miss M. E. Laing, whose experiments are embodied in a separate communication, amplified by the direct inferences rendered possible by our present observations, and also incidentally corroborated by numerous observations made in this laboratory in connection with other lines of investigation of soaps.

Technique.

Three ultramicroscopes were employed: the Zsigmondy-Siedentopf, the Jentzsch (kindly lent to us by Mr. Emil Hatschek), and the Zeiss Cardioid; the latter with heating appliance.

A heating arrangement was designed and ordered from Zeiss for the Zeiss-Siedentopf microscope shortly before the outbreak of war, but this had not been received. In some of our earlier experiments we employed a home-made cooling bath of ice water, in which the Zsigmondy-Siedentopf cell was immersed. Each form of ultramicroscope possesses serious disadvantages, and it is often necessary to use two forms as check, in order to find out whether observations refer to the inherent structure of the systems under investigation. In the Cardioid form, the whole layer being only 0·001 mm. thick, much of the soap layer lies within the range of influence of the containing silica walls above and below it. The original Siedentopf-Zsigmondy and the Jentzsch forms enable observations to be carried out free from the effects of the containing walls, but no heating arrangement was available, and in many cases it was a matter of great difficulty to retain a given portion or structure of the system under continued observation. Further, visibility was difficult when an opaque layer of soap curd intervened. All final observations were obtained with the Cardioid.

The heating arrangement used with the Cardioid, which consists of a film of platinum on the cover-glass, heated electrically, had to be repaired repeatedly, and the platinum renewed. For this reason the temperatures are not accurately measured, but they are fixed quite sufficiently for the present purpose by macroscopic observations.

The cinematograph camera was the comparatively inexpensive but satisfactory "Ensign" supplied by Houghton's, Ltd. By marking the position of the driving handle in relation to the shutter, it was possible to take exposures at any required interval from 1/10 second up to several hours. Of course, much of the finer detail, and many observations such as that of Brownian movement of small particles, was beyond the range of any but ocular observations with the highest powers of the ultramicroscope (Zeiss ocular No. 18); Zeiss apochromat N.A. = 0·78 (3 mm.). With the cinematograph and other cameras a Zeiss No. 2 projector was used. Some uncertainty was involved in focussing the cinematograph camera, as this had to be done by focussing on transparent paper in the gate of the machine before mounting the film in the camera. The illumination in all cases was provided by direct current arc taking 30–50 ampères.

Two devices which have been of the greatest assistance are of general application. The first was the insertion of a vertical illuminator, such as is used in metallography, in the tube of the ultramicroscope. By this means an image of the system under investigation is thrown on a screen so that it may be watched during the actual cinematographic or photographic experiments. The second was of service in studying the life history of various particles and fibres during their formation, ageing and disappearance. This was the joining up of the ends of the cinematograph film to make an endless band driven by motor so that it was projected upon the screen before the lantern again and again in rapid succession. The film could be passed backwards or forwards until doubtful points were cleared up.

Brownian Movement and Hydrolysis.

It is of advantage to discuss the Brownian particles first, in order that they may not distract attention from the main interest of the work.

One kind of particle that is almost invariably observed in soap sols, gels and curds is a product of hydrolysis. This type varies in size from particles visible to the naked eye down to those of very low ultramicroscopic dimensions. These particles are in a sense extraneous and an unessential part of the solution, since they are merely a solid product of hydrolysis which is regulated entirely by the low hydroxyl ion concentration in these soap systems.

Brownian movement is exhibited by two other constituents of soap solutions. Thus it is shown by portions of curd fibres which are not attached to any solid body, such as to a quartz cover-glass or to a network of other fibres.

Much more important are the innumerable milky-white particles which appear to be present in all these soap systems but usually just below the border line of visibility in the highest powers of the ultramicroscope. It is often only when the conditions are exceptionally favourable or in a particularly well illuminated portion of the field that they become just visible; then, however, their existence in immense numbers is undeniable. It is probable that this structural element, like the curd fibres, consists of neutral undissociated soap colloid. In the case of soap solutions that are just above their solidification temperature, sudden cooling serves to develop them into easily visible dimensions. In the case of the higher sodium soaps of the saturated fatty acids, some are often readily visible even above the temperature at which fibres appear, as is more fully described in the discussion below. In a more efficient ultramicroscope they would probably always be visible in all soap systems.

The Brownian movement has been of the greatest assistance in this ultramicroscopic study, since it affords a direct measure of viscosity of the solution and hence very often shows how much soap is still left in the solution. When we know from our experience of soap solutions that the solution itself is highly viscous, Brownian movement is found to be slight or altogether suppressed. The most rapid Brownian movement is attained in soap curds which have stood at room temperature until most of the soap has separated out, leaving only a thin aqueous fluid between the curd fibres. In such cases the larger particles are white, the smallest are purple, and the very rapid motion of the latter is rivalled by the smaller variety of the green particles.

The Brownian particles exhibit two very interesting varieties of movement. The first is when they collect in the surface of a soap-air interface and there carry out Brownian movement in two dimensions, with a vigour depending upon the viscosity of the soap solution in contact with them. Frequently such a surface is crowded with particles.

Another variety of Brownian movement has not been previously described. Very frequently, when a particle has come into contact with a curd fibre, it finds some difficulty in leaving again, although violent activity may still persist in one dimension, namely, up and down the length of the fibre. Sometimes such a particle shakes itself loose.

This peculiar movement, before it was properly understood, led to difficulties in interpreting the nature of various rectilinear spaces and boundaries into which, or out of which, Brownian particles did not seem to be able to move. This was found to be due to the difficulty of crossing the curd fibre which served as the apparent boundary. In this way sharply defined geometrical figures, occurring as the result of perhaps a chance network of fibres, might easily be mistaken for solid crystals.

Soap Solution and Soap Gels.

Both of these closely similar transparent systems are nearly clear in the ultramicroscope. Except when cooling has developed the neutral colloid into visibility in the form of white particles, the sols and gels usually contain no ultramicroscopic constituents other than a few Brownian particles. The ionic micelle is invisible. Bachmann's paper contains a number of observations with regard to the development of the neutral colloidal particles upon rapid cooling, and he labelled them "first and second solid phases."

The above applies to both potassium and sodium soaps. On the other hand, in the case of the hydrogen soap, cetyl sulphonic acid, the numerous white particles of neutral colloid are always prominent and very numerous; whilst the clear liquid in which they are contained exhibits a fine-grained shimmering activity, as if it were full of movement, although no particles are visible. Possibly this background effect is to be ascribed to the ionic micelle, but more probably it is due to amicroscopic particles of neutral soap.

In the case of sodium oleate gel we made several attempts to find out if any gel structure was visible. The difficulty is to eliminate the presence of the curd fibres. On one occasion a network of fibres was observed, which differed from the curd fibres, also present, in that they were much finer than, and a different colour from, the latter, and also that they had no fine loose ends. These fibres formed one continuous network of curved lines, like expanded sheet metal. When mechanical pressure was applied to one side, so that the whole flowed, this fine network flowed with it, the meshes widening or narrowing, but remaining otherwise intact, whereas the characteristic curd fibres curved and pulled themselves through the gel until they lay in straight lines down the current. This network is probably not the characteristic structure of gels, since the meshes are unexpectedly large, and we have observed gels exhibiting no visible structure. What does seem clear is the tendency towards a filamentous structure, which we believe is probably the general characteristic of soap gels as distinguished from sols. These filaments, however, must normally be amicroscopic.

A few extraordinary fibres were observed in sodium oleate gels. Some resembled a pure sine-wave curve continued with the utmost regularity in a line across the field. Others exhibited similar periodicity, but with numerous harmonics. In every case the surprising characteristic was that any part of one fibre was an exact replica in form and in structure of the corresponding part of all the other numerous waves of which the fibre was composed. Fig. 1 (Plate 10) is a photograph, obtained with about twenty minutes' exposure, which, however, gives but a faint impression of the remarkable detail observable in these fibres. In appearance the fibre consists of a nearly colourless gelatinous tube, containing white particles of different sizes, shapes and orientation, distributed in rhythmic patterns along the length of the tube. Possibly the curves are produced when the gel shrinks in the direction of the length of the fibres.

SOAP CURDS. FELTS OR PASTES.

1. *Sodium Salts of the Saturated Fatty Acids.*

In this series the laurate, myristate, palmitate and stearate were studied. The distinctive characteristic is that the curds are comprised of a felt of fibres which may be centimetres or inches in length, but which are usually of ultramicroscopic diameter. That is, these curd fibres are dependent upon dark ground illumination for their detection and give only diffraction lines from which their true diameter cannot be inferred. Sometimes the fibres appear to be definitely visible, that is, to be of microscopic diameter; but this is somewhat uncertain since in some cases such fibres can be shown to consist of bundles of parallel ultramicroscopic fibres. The "fibres" which are often visible to the naked eye and which may give the characteristic "feather" to curd soaps are certainly bundles of microscopic or ultramicroscopic fibres.

Surprising as it appears, this is apparently the stable condition of sodium soaps, even after standing for years; although, after this paper was drafted, we discovered that the sediment of the dilute solution of sodium palmitate which had stood for five years consists partly of fibres but partly also of crystals very similar to those of potassium stearate described below. Fig. 2 shows a specimen of this sediment from N/50 sodium palmitate which was introduced into the cardioid cell without warming. Further work will be required to decide whether these crystals are composed of acid or neutral soap and whether they appear within a reasonable time.

If the solution has been kept long enough in contact with glass, definite crystals of silicate are occasionally met with. As will be shown in other communications, the curd fibres exhibit solubility depending upon the temperature, so that they gradually disappear upon warming and are increased on cooling.

Zsigmundy and Bachmann have observed that on ageing the coarser fibres are developed at the expense of the finer ones, as would indeed be expected from consideration of the effects of the surface tension. They also observed that on ageing the fibrous structure became even more pronounced and exhibited less similarity to crystals or crystallites; this is probably due to the fact that the degree of hydration of the curd fibres has to readjust itself to the altered concentration of the residual mother liquor with which it is in contact. Fresh solutions of soap above the temperature at which fibres appear are not as clear as solutions that have had some time to settle before withdrawing a sample for investigation. This is presumably due to sedimentation of the products of hydrolysis.

(a) *Sodium Laurate* (concentration = 1·0 N).

Above 60° C. this solution is optically clear in the field of the ultramicroscope. On cooling slowly, long thin fibres of characteristic curvature are observed to grow into the field. These fibres appear to increase in length and diameter, and eventually, if the cooling is continued, become so numerous that a felt-like mass is obtained, in which it is no longer possible to distinguish individuals. This behaviour is illustrated in fig. 3. In many cases it appeared as though these fibres had attained their full length before becoming visible, and it seems probable that they must have existed previously, as long chains of molecules or aggregates, below the limit of visibility of the microscope. (This agrees with Zsigmondy and Backmann's impression of the pre-existence of sodium palmitate and stearate and oleate fibres in the optically clear solution.) In no single case were we able to observe the growth of one of these fibres from a nucleus. The fibres are so intertwined as to account for the rigidity of the solid soap. On heating again, the smaller fibres disappear, leaving a coarse network composed only of large fibres, which on further heating do not diminish in diameter, but appear to contract longitudinally from both ends, until they finally disappear, and the liquid becomes optically homogeneous. It was often observed that the shredded ends of these coarse fibres gave the impression that what had appeared to be a single fibre consisted in reality of bundles of fibres.

(b) *Sodium Myristate* (0·75 N).

This soap is very similar in its behaviour to sodium laurate, the fibres being possibly slightly coarser, and in the final state more matted.

(c) *Sodium Palmitate* 1·0 N *and* 0·25 N.

This solution becomes clear only above 90° C. On cooling, the field usually becomes full of small particles in fairly rapid Brownian movement (sometimes, however, there is only a lightening of the background). As the cooling progresses, the movement becomes less violent, probably owing to increasing viscosity. At about 75° there is again a rather sudden increase in the number of these particles (*cf.* Zsigmondy and Bachmann). We believe these particles to consist chiefly of neutral colloidal soap. (In 0·25 N solution no such particles were observed.) At 67° thick parallel fibres appear and from this temperature downwards they continue to grow and finally become so numerous that it is no longer possible to distinguish any structure in the dazzling white mass. These fibres are much straighter than laurate fibres, and judging by the amount of diffused light in their neighbourhood they must be of considerable thickness; in fact they can frequently be distinguished even in transmitted light. In 0·25 N solution parallel fibres were obtained by slow cooling; they radiated from definite centres when formed by rapid cooling after insufficient heating. In one particular case, where the specimen had been repeatedly warmed and cooled, and finally allowed to stand for some time, fibres were observed with the naked eye, radiating from a point and which were exactly similar to ordinary crystallites in their appearance. These "crystals" were probably formed as the result of evaporation. This would agree with an earlier observation of McBain and Salmon, where it was noticed that in the evaporation of a concentrated soap solution, at a certain definite concentration, small star-shaped crystals appeared on the sides of the vessel.

(d) *Sodium Stearate* 0·5 N.

This soap is very similar to sodium palmitate, but with the rather remarkable difference that the fibres are frequently "beaded" in appearance (fig. 4). This might be explained by their being crossed by other fine fibres if it were not for their absolute regularity. An alternative explanation is that they possess a spiral structure. This is sometimes supported by the fact that alteration of focus brings into view portions of the fibres which were previously invisible; but it is by no means certain that this is a correct explanation (*cf.* sodium oleate discussed above). It is possible that they may be due to particles held in position by the fibres.

2. *Sodium Salts of the Unsaturated Fatty Acids.*

(a) *Sodium Oleate* 0·6 N.

This solution is of special interest since it can be obtained at room temperature in the three forms, sol, gel, and curd, already described. Under the ultramicroscope the sol appears optically homogeneous. On cooling the curd results, and this appears very much like other sodium soaps, resembling most closely sodium stearate, the corresponding saturated fatty acid. The fibres are beaded in the same manner but to a much greater extent (fig. 5).

(b) *Sodium Rosinate* (*Abietate*).

The investigation of this specimen appeared to be of great importance in view of its very extensive employment in household soaps. The rosinate investigated was a specimen prepared by Miss K. M. Gibbins, by boiling the best W.W. rosin of commerce with sodium ethylate in dry alcohol. The sodium salt freed from alcohol should, therefore, have contained no appreciable amount of abietic anhydride, and should therefore be comparable with the completely saponified rosin usual in commercial soap.

It was found necessary to use a much more concentrated solution of this thoroughly saponified material than had been indicated by a preliminary experiment with the merely neutralised resin. In order to obtain an appreciable amount of separated rosinate on cooling, it was necessary to make the solution about 3·5 N. At the boiling point this appeared to consist of one liquid phase with a few ultramicroscopic particles in Brownian movement which was very slow on account of the high viscosity of the medium. On cooling, separation into two liquid phases took place, and on further cooling, each of these deposited large amounts of ultramicroscopic particles whose shape could not be directly inferred, except that they appeared decidedly granular, rather than spherical, on account of the asymmetry of the optical changes produced when focus and illumination were altered.

The important point to notice is that there are no fibres but merely irregular granules which have a tendency to arrange themselves into regular lines, like fine grained leather. The behaviour of sodium rosinate is rather like that of a sodium soap whose curd fibres are extremely soluble at the temperature of the experiment. The same explanation may hold for the 0·5 per cent.—1 per cent. gels of sodium palmitate and stearate in alcohol, in which Zsigmondy and Bachmann observed granules only.

Fibres were, however, obtained by the addition of common salt in the concentrated solution just described. In this case, one of the liquid phases continued to deposit granular particles whilst the other developed instead short inconspicuous rather straight fibres, very different from the luminous white fibres of the higher sodium soaps such as palmitate or oleate. The rosinate fibres differ from the other sodium soaps in being only a few hundredths of a millimeter in length, and they differ from potassium fibres in showing no tendency to twin.

3. *Potassium Salts of the Saturated Fatty Acids.*

The potassium soaps do not form rigid curds like the sodium soaps. Their ultramicroscopic appearance and structure is also quite different. There are no long curd fibres such as are characreristic of all sodium soaps. Their place is taken by short fibres which are never more than a few hundredths of a millimeter in length. Moreover these short fibres exhibit strong tendency to appear as twins.

Another fundamental difference is the fact that at room temperature, the stable form of potassium soaps is that of true crystals, the fibres being replaced by these small lamellar crystals as Zsigmondy and Bachmann have also clearly shown.

(a) *Potassium Stearate* (0·5 N).

Above 70° this solution is very similar to sodium palmitate, but below this temperature its behaviour depends upon the rate of cooling. We have spent a great deal of time in order to be quite certain that no structural elements are to be found other than those already mentioned. We are, however, satisfied that only three formations ever appear. The first is greatly enlarged Brownian particles of neutral soap, often in violent movement; the second is **V**-shaped twin crystals or fibres, frequently highly distorted, fig. 6; and the third and permanent form is constituted by the minute lamellar crystals. The appearance of this transition for one particular rate of cooling or ageing has been well shown in the diagrams of Zsigmondy and Bachmann.

At first we were somewhat sceptical with regard to the existence of these crystals, since similar formations are very readily produced by the interlacing of fibres. However, repeated observation of these heaps of crystals during heating shows that they liquefy (possibly to a crystalline liquid) whilst dissolving, and their contours remain smooth and closed even when they are altering and flowing freely. Often in the mass, some of the boundaries appear incomplete.

Very slow cooling gave the clue to the understanding of these systems. Under these circumstances, on cooling below 65° or 70°, only fine sharp twin crystals or fibres form, fig. 7. These steadily grow in length, their diameter remaining apparently rather less than that of sodium curd fibres; with age they become more and more deformed and build up an apparent network structure, which begins to appear in less than an hour after their first formation, fig. 8. On standing for a day or so they begin to be transformed into the stable crystal leaflets, fig. 9, although, like Zsigmondy and Bachmann, we have not been able to observe the actual process, which requires several days at room temperature for completion.

Upon rapid cooling the phenomena take place with such bewildering rapidity, complicated by Brownian movement, that they are much less easy to disentangle. However, it seems clear that the first effect is the rapid increase in size and numbers of particles of neutral soap, together with agglomerations of these particles, the whole being in movement. Highly distorted, but not recognisable V-shaped fibres and pieces of fibre rapidly appear, fig. 10. These grow, rather slowly, at the expense of the particles of neutral soap. Often a fibre that has been motionless for some time, moves with a jerk across the field and either attaches itself to a fibre or arranges itself with respect to it, until the fibres have become interlaced to form an apparent network which is ultimately replaced by the tubular crystals.

The cloud of larger Brownian particles could be made to appear at any stage of the slow cooling just described, by causing a sudden cooling to take place. It would therefore seem that these fibres possess a true solubility for each temperature, and that sudden lowering of temperature deposits from solution a certain amount of soap, which then redissolves to crystallise out as fibres.

(b) *Phenol and Water.*

Several observations were made with mixtures of phenol and water above and below the critical temperature in order that we might be aware of the ultramicroscopic picture presented by the appearance of a new liquid phase. In every case, no matter how slow or rapid the cooling, numbers of points or round discs of light appear all over the field. This general appearance was wholly different from anything seen in any soap system investigated. A complete description of the phenomena observed in such cases has been published from Zsigmondy's Laboratory by Von Lepkowsky.*

(c) *Potassium Palmitate* 1·0 N.

This soap is identical in its behaviour with the stearate, the twin fibres being perhaps less clearly defined and the final structure less easily resolved.

4. *Hydrogen Soap. Cetyl Sulphonic Acid.*

Cetyl sulphonic acid, $C_{16}H_{31}SO_3H$, is remarkable as being a hydrogen soap and it is of quite special interest because hydrolysis in this case is out of the question.

The microscopic appearance is rather similar to that of potassium soaps, in that innumerable glittering crystals appear to exist in the curd.

A 0·5 N solution prepared as described by Reychler was full of colloidal particles even at temperatures well above that at which curd fibres appeared. The colloidal particles were prominently visible, but in addition the clear intervening liquid exhibited a remarkable shimmering effect as if in intense fine grained movement. The impression given is that two kinds of colloidal particle are present, one that is readily visible and another which is just upon the border-line of ultramicroscopic visibility but in extremely active Brownian movement. If so, the large particles would be colloidal sulphonic acid, analogous to neutral colloid in soap solutions, and the fine intense movement might just possibly be due to ionic micelle.

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* 'Zeitschr. physikal. Chem.,' vol. 75, p. 608 (1911).

On gradual cooling, curd fibres appear. These fibres are short like those of potassium soap, and they also exhibit a tendency to form twins, although in this case the angle of twinning is generally obtuse and the twins are not so well developed. A distinction between these fibres and those of sodium soaps is that they are much finer, so much so that in some cases it would be impossible to detect them were it not for their being overloaded with large Brownian particles like large beads on a thread. Such particles are however in incessant vibration, transverse as well as up and down the thread. Fig. 11 taken on a process plate, exposure 12 seconds, appears somewhat fogged owing to the marked Brownian movement.

Upon standing for some days the fibres show a tendency to develop and aggregate into an apparent network as in the case of potassium soaps. Further, the shimmering appearance is less marked in the dark spaces away from the fibres although quite as pronounced as before in the neighbourhood of the groups of fibres where the Brownian particles tend to assemble.

In further analogy with potassium soaps we have found that tabular crystals appear after standing some days or weeks. These crystals are often very difficult to see on account of their extreme thinness, which of course was much less than 1/1000 mm. Their crystal form is better developed than in the case of potassium soaps.

Owing to their extreme thinness some of the smaller of these crystals, which are floating in the liquid out of contact with the walls of the cardioid cell, exhibit extraordinary and constant movement. They bend, rotate, and even vibrate transversely with very rapid movement while swimming through the solution. Upon heating, such a moving crystal curls up at both ends, the thickened ends rapidly disappearing; meanwhile the crystal tends to bend spasmodically, forming well-marked obtuse angles in addition to the constantly varying flat curves. The temperature at which the curled-up crystal finally disappears is higher than that at which the fibres vanish; just as in the case of the potassium soaps and in accordance with the predictions of the phase rule for the relative stability of the two phases. Fig. 11 shows such a "crystal" or "liquid crystal" in rapid transverse vibration, and moving freely in the liquid. The photograph distinctly shows very nearly the maximum curvature at a particular instant of vibration.

General Discussion.

Summarising our knowledge of sodium palmitate solutions derived from the work of Chevreul, Krafft, and his co-workers, and papers from this laboratory, especially those of Taylor, Salmon, Laing and Titley, we know that at 0° C. sodium palmitate is very insoluble, separating from solution practically quantitatively in the form of heavily hydrated curd fibres and leaving behind nearly pure water. There is an inappreciable amount of any other colloidal or ultramicroscopic form of soap present in the solution, since, on filtering, practically pure water comes through, and ultramicroscopic observations show clearly that there is only one structural element, namely, these curd fibres.

At 100° C., on the contrary, sodium palmitate is extremely soluble, and although dilute solutions contain crystalloidal matter, concentrated solutions consist chiefly of neutral colloidal sodium palmitate, together with sodium ion and colloidal ionic micelle, which contains part of the neutral colloid. Here practically all the soap is in colloidal form with, say, about one-half of it in the form of neutral colloid. All this colloid, whether neutral soap or ionic micelle, is invisible in the ultramicroscope. Upon gradual cooling, towards 70°, more and more Brownian particles appear. Zsigmondy and Bachmann considered that these were hydrolysed soap. This, however, can hardly be the case since hydrolysis, which has been directly measured, diminishes instead of increasing on cooling. They based this conclusion upon an observation that a small amount of sediment from similar solutions of potassium palmitate and stearate, after "drying," melted at about 100° below the melting point of the pure dry salts. We have shown in an earlier communication that only a part of the water can be removed from soap by drying at 100° *in vacuo*, so that their specimens necessarily contained water. Again, their sediment must have included the small but definite amount of acid soap which does result from hydrolysis, and which is usually present in the form of quite coarse particles. Miss Laing has shown by direct analysis that the curd fibres consist of hydrated neutral soap.

On cooling below 70° the tendency towards definite orientation of the colloid in the sol becomes so pronounced that definite fibres begin to appear. At each temperature there is a definite concentration of soap left behind in solution, the fibres then exhibiting a definite solubility at each temperature. As the temperature is further lowered, more and more fibres separate out. These must be found at the expense of all the other forms of soap in the solution until we arrive at the wet felt of hydrated curd fibres at 0° described above.

This description applies to all the sodium soaps, bearing in mind that the stearate and behenate are more insoluble, and that the oleate, myristate, laurate and rosinate are more soluble, and that the latter contain more crystalloidal matter in their solutions.

This description also applies, in some measure, to the corresponding potassium soaps, remembering that these are more soluble than the sodium soaps, and that the curd fibres areonly a few thousandths or hundredths of a millimetre in length, instead of being perhaps many centimetres, and that, finally, upon standing for a short time at room temperature, the soap recrystallises in the form of innumerable thin flat crystals of microscopic dimensions.

It is important to note that we have found that commercial sodium soaps also contain, as sole structural constituent, hydrated curd fibres, with enmeshed liquor, which is a sol or more frequently gel of the various more soluble soaps and salts present.

It is also of great interest to note that in the only case here investigated the fibres of palmitate and rosinate separate out largely independent of each other instead of forming one new kind of mixed fibre. Other direct corroborative evidence will be given in Miss Laing's communication, to which we have several times referred.

Summary.

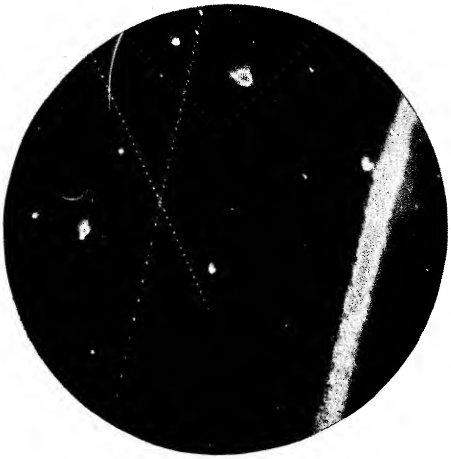
1. The ultramicroscopic observations of Zsigmondy and Bachmann have been confirmed, interpreted and extended. Their observations referred almost entirely to soap curds, not gels or sols, for the latter usually exhibit in the ultramicroscope nothing except Brownian particles, and that only under definite conditions.

2. The cinematograph has been employed as an aid in elucidating the formation and disappearance of the various structures observed.

3. Curds of sodium soap consist of a felt of hydrated fibres enmeshing and in equilibrium with a soap sol or gel of definite concentration, the solubility rising rapidly with temperature. The individual fibres may be many centimetres long, but they are barely of microscopic diameter.

4. Potassium soap solutions, on cooling, first develop fibres which are similar to those of the sodium soaps, except that they are only a few hundredths of a millimetre in length, and that they have a strong tendency to form twins. The stable condition at room temperature is, however, the formation of innumerable tiny lamellar crystals of hydrated soap.

5. The hydrogen soap, cetyl sulphonic acid, is similar to the potassium



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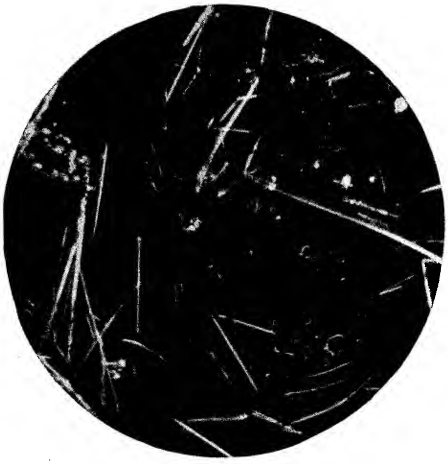

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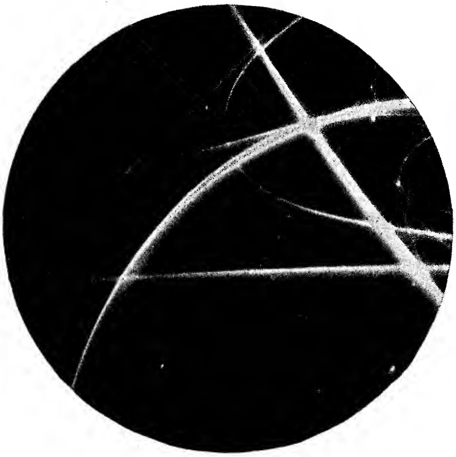

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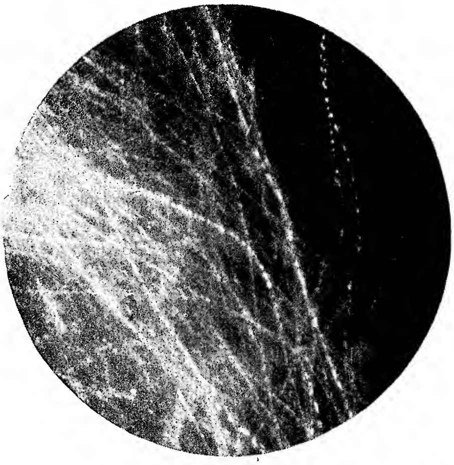

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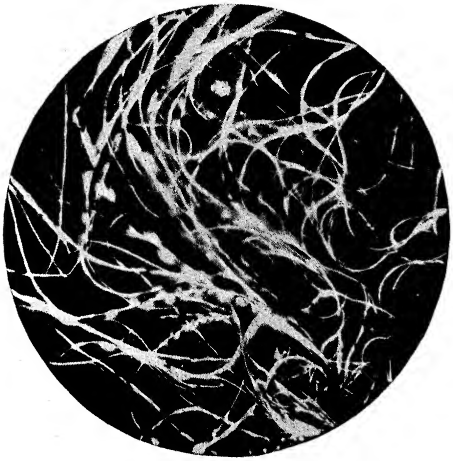

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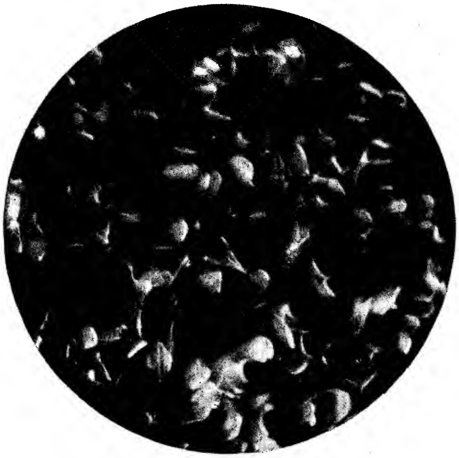

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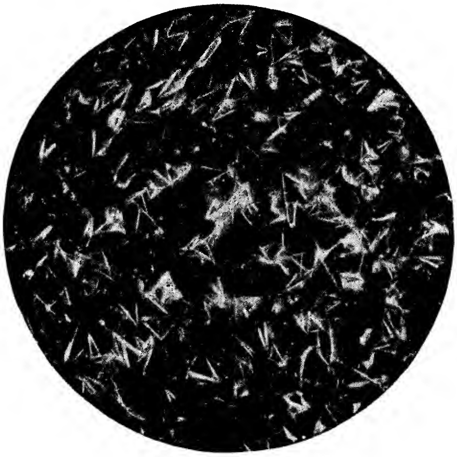

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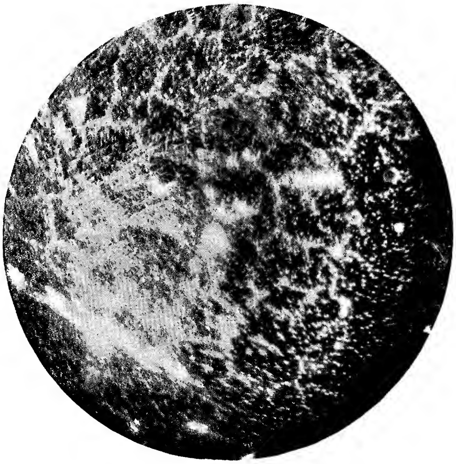

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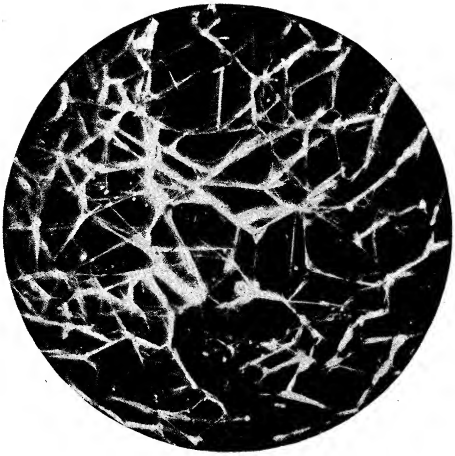

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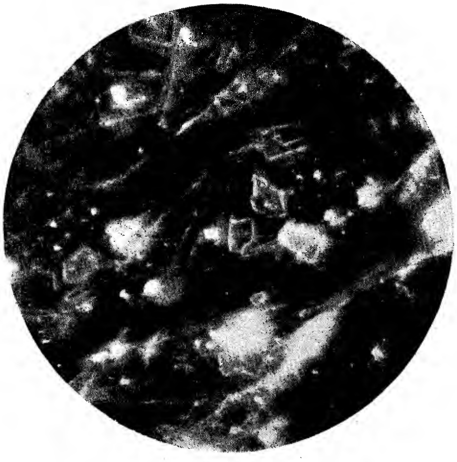

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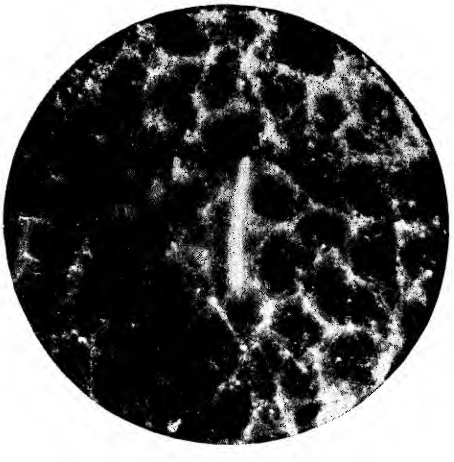

11

soaps, but the particles of colloidal cetyl sulphonic acid are very much more prominent.

In conclusion, we desire to express our thanks to the Research Fund of the Chemical Society and to the Colston Society of the University of Bristol for grants with which the pure materials were purchased.

DESCRIPTION OF PLATES 10 AND 11.

Figs. 1 and 5, 0·6 N Na oleate; fig. 2, 0·2 N Na palmitate; fig. 3, 1·0 N Na laurate; fig. 4, 0·5 N Na stearate; figs. 6, 7, 8, and 9, 0·5 N K stearate; figs. 10 and 11, 0·5 N cetyl sulphonic acid. Figs. 2–11 refer to curds. Magnification ×500 in figs. 1, 2, 5, 7, 8, and 11; ×600 in figs. 3, 4, 6, 9, and 10.

The Transmission of Electric Waves around the Earth's Surface.

By H. M. Macdonald, F.R.S.

(Received January 10, 1921.)

In the 'Proceedings,'* Prof. G. N. Watson discusses the effect of a perfectly conducting layer in the atmosphere at a uniform height above the earth's surface on the transmission of electric waves round the earth. The mathematical treatment adopted by him assumes that the time factor $e^{-\iota k C t}$ can be removed from all the equations, and that the analytical results thus obtained represent the effect of a simple oscillator placed near the earth's surface. The assumption that the time factor can be removed is equivalent to assuming that a steady state of oscillations exists in the space between the two spheres, such that at the end of a period the amplitudes of the electric and magnetic forces are identical at each point with the values they had at the beginning of the period. Now, when the surfaces of both spheres are perfectly conducting, no energy is transmitted across either surface, and therefore, if there is a steady state of oscillations in the space, the total energy in the space must be constant. When there is an oscillator in the space emitting electric waves, there is a finite amount of energy radiated from the oscillator in each period, and therefore the total energy in the space does not remain constant; it follows that in such a case there is no steady state of

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* 'Roy. Soc. Proc.,' A, vol. 95, p. 546.

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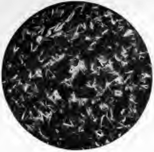

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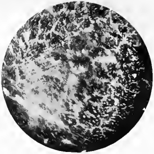

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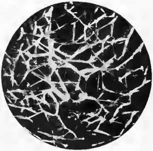

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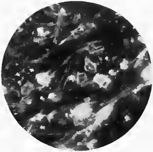

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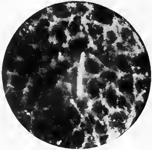

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DESCRIPTION OF PLATES 10 AND 11.

Figs. 1 and 5, 0·6 N Na oleate; fig. 2, 0·2 N Na palmitate; fig. 3, 1·0 N Na laurate; fig. 4, 0·5 N Na stearate; figs. 6, 7, 8, and 9, 0·5 N K stearate; figs. 10 and 11, 0·5 N cetyl sulphonic acid. Figs. 2–11 refer to curds. Magnification ×500 in figs. 1, 2, 5, 7, 8, and 11; ×600 in figs. 3, 4, 6, 9, and 10.